Dr Bright

CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH

OTTAWA

MINERAL SCIENCES DIVISION

INTERNAL REPORT MS-65-114

THE THERMAL DECOMPOSITION OF PYRITE

by

A. W. Coats and Norman F. H. Bright

Prepared for submission for publication in the
"Canadian Journal of Chemistry"

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October 19, 1965

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Mineral Sciences Division,
W.R. Inman, Acting Chief.

555 Booth Street,
Ottawa 4, Ontario,
December 15, 1965.

Dr. A.W. Coats,
High-Temperature Chemistry Division,
Central Electricity Research Laboratories,
Cleave Road,
Leatherhead, Surrey,
England.

Dear Tony:

I am enclosing for your interest and retention three copies of the paper on the decomposition of pyrite that I have today submitted to the Canadian Journal of Chemistry for publication. A copy of the letter to the Editor is also enclosed for your interest.

The more extended research report on the same subject that your wrote before you left for home, and on which this paper is based will, I hope, shortly be typed and printed. When copies are available, I will send you some.

May I take this opportunity to wish you and Heather all the very best for Christmas (if this reaches you in time) and, in any case, for the New Year.

Yours very sincerely,

Norman F.H. Bright,
Head,
Physical Chemistry Section.

Encl. 3

NFHB/af

Mineral Sciences Division,
W.R. Inman, Acting Chief.

555 Booth Street,
Ottawa 4, Ontario.
December 15, 1965.

Dr. J. A. Morrison,
Editor, "Canadian Journal of Chemistry",
National Research Council of Canada,
Sussex Drive,
Ottawa 2, Ontario.

Dear Dr. Morrison:

I enclose three (3) copies of a manuscript entitled "The Thermal Decomposition of Pyrite" by Dr. A.W. Coats and myself, which we wish to submit for consideration for publication in the "Canadian Journal of Chemistry". The paper describes work done by Dr. Coats during the tenure of an N.R.C. Post doctorate Fellowship in 1964-1965; the work was done in the Mines Branch under my direction. As Dr. Coats has now returned to England, it would be convenient if any correspondence relating to this manuscript should be directed to me.

I would be glad to be assured of your safe receipt of this manuscript.

Yours very truly,

Norman F.H. Bright,
Head,
Physical Chemistry Section.

Encl. 3

MINES BRANCH

Mineral Sciences Division

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(Author) A. W. Coats and Norman F. H. Bright

TITLE: THE THERMAL DECOMPOSITION OF PYRITE

(Date) October 19, 1965

Internal Investigation Report No. MS-65-114

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Mineral Sciences Division Internal Report MS-65-114

THE THERMAL DECOMPOSITION OF PYRITE

by

A. W. Coats* and Norman F. H. Bright**

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ABSTRACT

The kinetics of the thermal decomposition of purified pyrite to pyrrhotite and sulphur in a dynamic argon atmosphere have been studied over the temperature range 600° to 653°C. The reaction was followed by the rate of weight loss as indicated by a quartz spring balance and also by the rate of progression of the pyrite/pyrrhotite interface into a cylindrical, compressed, polycrystalline pellet. The temperature coefficient of the reaction was found to be 69.5 ± 5.9, 64.7 ± 3.3 and 66.9 ± 5.1 kcal $mole^{-1}$, when the results were processed in three different ways. The pyrite/pyrrhotite interface was found to progress at a linear rate into the pellet at a given temperature; equations were derived to express the variation of reaction rate with temperature. Attempts to follow the early nucleation stage of the decomposition, using massive mineral crystals, proved unsuccessful.

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INTRODUCTION

The thermal decomposition of the mineral pyrite (FeS_2) to yield pyrrhotite ($Fe\ S_{1+x}$) and sulphur has been made the subject of many investigations (1 to 13); this work has recently been reviewed by Kullerud and Yoder (1). Most studies have been made by measuring sulphur vapour pressure values (p_S) under equilibrium conditions over a range of temperatures. The enthalpy, ΔH, of the reaction, obtained from these measurements, has given values ranging from 39 to 104 kcal $mole^{-1}$ for various investigators, most values lying in the 65-85 kcal $mole^{-1}$ range. Most workers employed static conditions at less than one atmosphere pressure; Kullerud and Yoder (1), however, extended their measurements to higher pressures. The only investigation to be made under the dynamic conditions of a flow of inert gas appears to be that of Udintseva and Chufarov (12), who used both single crystals and polycrystalline cubes of pyrite.

The difficulties associated with the study of this reaction arise from two sources: (a) variability of composition of the resultant pyrrhotite, which is a non-stoichiometric body; Bog and Rosenqvist (9) expressed the reaction by the equation:

$$\left(\frac{2}{1-x}\right)\ FeS_2 \longrightarrow \left(\frac{2}{1-x}\right)\ FeS_{1+x} + S_{2(g)} \qquad \text{(Equation 1)}$$

for temperatures of 500° to 550°C, where x varies with temperature. Wunderlich (13) has pointed out that the degree of association of the sulphur also varies with temperature, higher pressures and lower temperatures of

reaction favouring the formation of S_8 and S_6 molecules over the S_2 indicated in the above equation.

In the present study, the conditions employed were those of constant gas flow similar to those that might be expected to obtain in an industrial manufacturing process for sulphur from pyrite. The aim of the work was to determine the kinetic parameters for the reaction of small polycrystalline cylindrical pellets of pyrite that would approximate in size the pieces of ore that would be used in the industrial process. In addition, this type of study was amenable to the same type of treatment analytically as that employed by McKewan (14) in the reduction of iron oxide pellets by hydrogen.

Initially, an attempt was made to study the nucleation processses occurring in the very earliest stages of the decomposition; no success, was, however, achieved in this objective. This work is mentioned in the Appendix.

EXPERIMENTAL TECHNIQUE AND RESULTS

The pyrite used in this work was a mineral sample from Eastman, Quebec. It was crushed, washed with dilute acid to remove any pyrrhotite, and then with water. The product (-40+100 mesh) was found to contain an appreciable amount of quartz. Accordingly, it was crushed to -200 mesh and the quartz removed as far as possible by heavy-liquid separation with tetrabromoethane. The final product, on analysis, corresponded to the formula $Fe\,S_{1.99}$; spectrographic analysis showed no significant impurity other than 0.3% Si, presumably as unliberated quartz.

The powder was pressed into cylindrical pellets of 0.25 in. diameter and height at 160,000 lb in^{-2}. The pellets weighed approximately 0.86 g., corresponding to a bulk density of about 4.1 g cm^{-3}. The apparatus in which the decomposition was studied consisted of a vertical quartz tube, a portion of which was heated by a Kanthal-wound furnace. Temperatures were maintained constant in the hot zone of the furnace to within $\pm$ 0.5°C, both in respect of location and of time. Samples were suspended in a light quartz stirrup at the end of a fine platinum wire, the upper end of which was attached to a calibrated quartz helical spring of sensitivity 5.39 cm g^{-1}. This spring was well above the top of the furnace and was, in turn, attached to a fine gold chain that was used for raising and lowering the sample by means of a suitable windlass mechanism. The extension of the spring was measured with a cathetometer. Sample temperatures were measured with a Pt : Pt 10% Rh thermocouple, sheathed in a fine quartz tube and placed not more than 0.25 in. below the sample and still well within the hot zone of the furnace. Argon flows of approximately 180 ml min^{-1} were used in the decomposition runs. The gas flow was maintained for 10 minutes before the pellet was lowered into the hot zone of the furnace; at the completion of a run, the sample was raised out of the hot zone and the gas flow maintained for 15 minutes before opening the apparatus.

Pellets were sectioned laterally, mounted and polished by the usual metallographic procedures. A partly-decomposed pellet exhibited a well-defined reaction interface having surfaces parallel to the external faces of the pellets. The diameter of the unreacted material was measured

at two locations at right angles on both top and bottom faces of the sectioned surface; the mean of these four values was taken to represent the extent to which the decomposition had proceeded. Cathetometer readings were taken at regular 5-minute intervals, so that the change in reading formed a measure of the bulk rate of decomposition.

The results were treated in two ways:

(a) Straight lines were obtained when the diameter of unreacted pyrite was plotted against time for a given temperature. An Arrhenius plot of $\log_{10} k_0$ against $\frac{1}{T°K}$, where k_0 is the velocity of advance of the interface in cm min^{-1} at a temperature of T°K, also gave a straight line. Least squares treatment was applied to this plot to obtain the equation of the best line through the points. The equation obtained was:

$$\log_{10} k_0 = 14.3 - \frac{15.18 \times 10^3}{T} \qquad \text{(Equation 2)}$$

(b) In McKewan's treatment (14), Equation 3 was assumed and, from it, Equation 4 was derived for spherical and cylindrical pellets with equal height and diameter:

$$\frac{dw}{dt} = k_1 A \qquad \text{(Equation 3)}$$

$$r_0 d_0 \left[1 - (1 - R)^{1/3}\right] = k_2 T \qquad \text{(Equation 4)}$$

where $\frac{dw}{dt}$ = rate of weight loss,

A = interfacial area between reactant and product,

r_0 = initial radius of pellet,

d_0 = initial density of pellet,

k_1 and k_2 = rate constants,

t = time,

R = fraction of reactant decomposed at time t

$$= \frac{\text{\% wt lost at time t}}{\text{\% wt lost at end of reaction}} \qquad (0 < R < 1)$$

In the present work, results were available to test the validity of Equations 3 and 4. In Equation 3, $\frac{dw}{dt}$ is directly proportional to the difference in successive cathetometer readings (Δx), taken at 5-minute intervals. A, the area of the interface between the pyrite and the pyrrhotite, is directly proportional to the square of the diameter (d^2) of the unreacted pyrite. Thus, a plot of Δx against d^2 for various temperatures should give a series of straight lines of slope k_1, where k_1 varies with temperature according to an Arrhenius equation. Again, applying a least squares fit to the values of $\log k_1$ plotted against $\frac{1}{T°K}$, the following equation was obtained:

$$\log_{10} k_1 = 12.8 - \frac{14.14 \times 10^3}{T} \qquad \text{(Equation 5)}$$

In Equation 4, values of R can be calculated from the weight of the pellet at a known time; this can be obtained either by direct weighing after a known reaction time or, alternatively, by computation from the

cathetometer readings. In this work, the former method was used. In the calculation of R, a value of 23.0% was taken as the total percentage weight loss in the reaction. The use of this value will be further commented upon later. Plots of $\left[1 - (1 - R)^{1/3}\right]$ against t gave straight lines of slope k_2, where k_2 varies with temperature according to an Arrhenius equation. As in the other cases, the application of the least squares method to the plot yielded the equation:

$$\log_{10} k_2 = 14.0 - \frac{14.63 \times 10^3}{T} \qquad \text{(Equation 6)}$$

DISCUSSION OF RESULTS

A calculation of the activation energy (E) from Equations 2, 5 and 6 gave the following results:

Method	E (kcal mole^{-1})
From diameter-time plot (Eq. 2)	69.5 $\pm$ 5.9
From area-of-interface plot (Eq. 5)	64.7 $\pm$ 3.3
From weight-loss plot (Eq. 6)	66.9 $\pm$ 5.1

The tolerance values quoted here were calculated for 90% confidence limits (15). From these results, it would appear that there is no significant difference in the value of E obtained from the three different plots.

In terms of absolute rate theory, where the rate constant k_3 is given by the equation:

$$k_3 = \frac{kT}{h} e^{\Delta S/r_e - \Delta H/RT} \qquad \text{(Equation 7)}$$

where the symbols have their usual significance, the value of E should be equivalent to ΔH. A comparison of the values obtained in the present work with those of earlier workers shows that the values of Bog and Rosenqvist (9) and of D'Or (5) fall within the 90% confidence limits obtained in this work.

Of the two methods used to determine the kinetic parameters of the reaction, that based on the direct measurement of the unreacted material appears to be simple to perform and involves no assumptions. The method can show whether the interface is advancing at a linear rate; however, the conducting of many experimental runs would be required. The method based on the work of McKewan, on the other hand, can be evaluated from far fewer experiments, since the weight changes can be obtained directly from the changes in the extension of the quartz spring or from some similar method. However, this method does incorporate a number of assumptions, e.g., that the rate is proportional to the interfacial area (Equation 3), and that the stoichiometry of the reaction is exactly known. A complete verification of the validity of Equation 3 would require practically the same quantity of results as would be needed for the former method; however, if Equation 4 is found to hold, then this would constitute a verification of the validity of Equation 3. In this particular reaction, the exact stoichiometry is <u>not</u> known since the composition of the resultant pyrrhotite is a function of temperature. In this work, the value of 23.0% decomposition, which was taken as representing the end point of the reaction, had to be an approximation. This was based upon the form of the

decomposition/time curves and showed that the reaction was completed after 75 minutes at the highest temperatures studied, and that the sample weight at this time corresponded to a 23.0% loss. This value of 23.0% would imply a formula approximating to Fe_7S_8 for the reaction product, pyrrhotite. This is reasonable when the known range of composition of this compound is considered.

CONCLUSIONS

1. The temperature coefficient of the decomposition of pyrite in a dynamic argon atmosphere is 69.5 ± 5.9, 64.7 ± 3.3 and 66.9 ± 5.1 kcal $mole^{-1}$ when the experimental results are processed in three different ways.
2. The equations of McKewan can be used to represent this decomposition reaction.
3. The pyrite/pyrrhotite interface advances at a linear rate; equations were obtained expressing the variation of the reaction rate with temperature.

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2. One of us (A. W. C.) wishes to express his thanks to the National Research Council of Canada for the grant of a Postdoctorate Research Fellowship.

APPENDIX

Preliminary Investigation of the Nucleated Decomposition of Natural Pyrite Crystals

At the commencement of this investigation, it was hoped to be able to study the decomposition of pyrite by investigating the rate of development of nuclei of decomposition on the surfaces of crystals of the mineral and also the rate of growth of these nuclei, possibly in various crystallographic directions. It was then hoped to be able to correlate this information with the bulk rate of decomposition as determined by other methods, described in the main portion of this paper. There was also the possibility that the rates of decomposition in various directions could be correlated with the crystal structure in the same way as was done by one of us (N. F. H. B.) for the dehydration of certain salt hydrates several years ago (16).

The study was conducted on small natural pyrite crystals (approx. 0.25 in. cubes). The crystals were heated in vacuo and observed with a low-power microscope. No individual nuclei could be observed up to a temperature of 550°C but, on removal of the crystal from the vacuum enclosure after cooling, it was obvious that some decomposition had taken place, since the crystal was then black in colour in contrast to its original brassy hue. Oblique illumination of the crystal with coloured light also failed to reveal the formation of any discrete nuclei on heating.

On closer examination, blue-grey areas could be observed which appeared at first to increase and then to decrease in size. This effect could

possibly be due to interference colours caused by a very thin film of pyrrhotite over the surface of the crystal, the appearance and disappearance of the colours being associated with the varying film thickness.

Other problems encountered with the use of natural pyrite crystals were: inhomogeneity of the interior of the crystal, the presence of impurities and the variation in weight, size and composition from crystal to crystal. These problems could best be eliminated by using polycrystalline, pelletized material. As no discrete nuclei had been observed, the aim of the work thereafter was directed towards studying the kinetics of the post-nucleation reaction.

This preliminary work did, however, imply that the surface of the crystal was very quickly covered by a thin film of reaction product and that the formation and growth of individual nuclei was unlikely to be the rate-controlling step in the decomposition, but rather the rate of movement of the pyrite/pyrrhotite interface into the crystal.

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